

## ENHANCED MERCURY CONTROL IN COAL-FIRED POWER PLANTS

### Field

5 The present invention relates to a method of reducing the mercury emissions for coal-fired power plants.

### Background

10 The United States Environmental Protection Agency (EPA) in its Utility Air Toxins Report to Congress-February 1998 concluded that "mercury from coal-fired power plants is a serious concern. Power plants account for about 52 tons of annual manmade mercury emissions in the country." The report stated that EPA has been unable to identify any currently feasible, commercially available technology for reducing these emissions. It recommends "further evaluation of  
15 potential control strategies" (see [www.epa.gov/region2/health/mercury.htm](http://www.epa.gov/region2/health/mercury.htm)).

20 The United States Department of Energy (DOE) indicated that it "wants to develop a wider array of mercury control options for power plants that can reliably reduce emissions by 50 to 70% by 2005 and 90% by 2010." (See [www.netl.doe.gov/publications/press/2001/tl\\_mercurysel2.html](http://www.netl.doe.gov/publications/press/2001/tl_mercurysel2.html))

A variety of previous attempts have been made to capture mercury.

25 Ide et al describe the conversion of mercury into mercuric chloride via addition of acidic chlorine containing material, especially hydrogen chloride, into mercury-containing gaseous emissions (see Ide, Akio et al. 1988. "Process for Cleaning Mercury-Containing Gaseous Emissions". United States patent 4,729,882). This mercury removal technique requires massive hydrogen chloride injection into mercury containing flue gas, at HCl levels of 500 to 1500 ppm, which would  
30 result in excessive corrosion of coal fired power plant steel components. Furthermore, combination of this technique with subsequent hydrogen chloride/mercuric chloride containing flue gas in a wet flue gas desulphurization

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system (FGD) containing alkali for purposes of sulphur dioxide adsorption from flue gas as a sulphite, bisulphate, bisulphate, or sulphate would result in unacceptable consumption of alkali scrubbing chemicals by the adsorbed hydrogen chloride. Therefore, this technique for mercury control is not believed  
 5 to be commercially viable in coal-fired power plants.

Felsvang et al describe mercury absorption between 110-170°C in the presence of chlorides, especially hydrogen chloride and alkaline "basic absorbent" introduced as an aqueous aerosol suspension (Felsvang, K et al. 1995. "Method  
 10 for Improving the Hg-Removing Capability of a Flue Gas Cleaning Process". United States Patent No. 5,435,980). This technique requires the use of substantial expensive capital equipment foreign to conventional coal fired power plants. It does not utilize existing flue gas desulphurization equipment. Furthermore, alkaline sorbent designed to remove mercuric chloride is partially  
 15 wasted by hydrogen chloride unreacted with mercury. Finally, its excessive use of hydrogen chloride, especially at 110-170° is certain to cause highly undesirable corrosion of steel containing surfaces in coal-fired power plants to iron chlorides.

Meichen and Pelt al describe the use of precious metals, especially gold, to catalytically convert elemental mercury  $\text{Hg}^0$  to mercuric chloride  $\text{HgCl}_2$  in flue gas (Meischen, S. and J. Van Pelt. 2000. "Method to Control Mercury Emissions from Exhaust Gases". United States patent 6,136, 281). This process is limited to  
 20 oxidation of mercury to mercuric chloride in flue gas below 300°C due to undesirable loss of gold as volatile gold trichloride. This technique requires the  
 25 use of substantial expensive capital equipment foreign to conventional coal fired power plants plus the use of very expensive precious metal catalysts.

Biswas and Wu describe the irradiation of solid particles with light, especially  
 30 ultraviolet light, to induce catalytic photo-oxidation of mercury to forms capable of being adsorbed by solid particles (Biswas, P. and C. Wu. 2001. "Process for the

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Enhanced Capture of Heavy Metal Emissions". United States Patent No. 6,248,217). Unfortunately, this technique requires the use of substantial expensive capital equipment foreign to conventional coal fired power plants plus the use of consumable metal catalysts.

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Amrhein describes the use of existing wet flue gas desulphurization systems to capture oxidized mercury in a manner which inhibits undesirable partial conversion of adsorbed oxidized mercury back to volatile elemental mercury (Amrhein, Gerald T. 2001. "Mercury Removal in Utility Wet Scrubber Using a Chelating Agent". United States Patent No. 6,328,939). The disadvantage of this method is that it requires effective but expensive chelating agents with potential problems due to chelation of scrubber metal components with chelates.

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Previous publications have indicated that alkaline fly ash containing solids have an affinity for mercury capture. For instance, Galbreath and Zygarlicke have shown that subbituminous coal ash can capture a portion of mercury in a flue gas (Galbreath, Kevin C. and Christopher Zygarlicke. 2000. "Mercury Transformations in Coal Combustion Flue Gas". Fuel Processing Technology. 65-66, pages 289-310, @ page 304). They also indicated that hydrogen chloride

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spiking of flue gas inhibited mercury capture by alkaline solids, such as calcium hydroxide or alkaline fly ash by neutralizing the alkaline sites able to complex mercury, especially oxidized mercury. United States Patent No. 6,250,235 issued to Oehr and Yao describes the addition of a fossil fuel and additive in a combustion zone to achieve the following results alone or in combination:

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accelerated combustion, desulphurization, nitrogen oxides emission reduction, pozzolanic or cementitious products production or combustor anti-fouling (Oehr, Klaus H. and Felix Z. Yao. 2001. "Method and Product for Improved Fossil Fuel Combustion". United States Patent No. 6,250,235). This is achieved by fusing alkali, such as calcium oxide, to coal ash and sulphur, while the coal is burning, via a flux. Full scale testing of this patented method, using bituminous coal in a 100 megawatt power plant, resulted in 45% reduction of mercury emissions as

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compared to testing without the use of above fuel additive. X-ray analysis of the resulting fly ash indicated that the normally acidic bituminous fly ash had been converted to an alkaline form containing alkaline cementitious crystals not unlike those found in subbituminous or lignite based fly ash as well as containing small amounts of alkaline calcium oxide and calcium hydroxide.

It is also well known that elemental mercury ( $\text{Hg}^0$ ) can be absorbed by activated carbon. Adsorption improves as the temperature of the carbon is reduced or if the carbon is impregnated with halogen species, such as iodine or chlorides and/or sulphides. Unfortunately the use of activated carbon requires extremely high carbon to mercury ratios e.g. 3000 – 100,000 to 1 carbon to mercury weight ratios. Injection of activated carbon into the cool zones of coal combustors ahead of the ESPs, FFs or BHs, results in unacceptable contamination of coal ash with carbon for purposes of ash recycling into cement/concrete applications.

Finally, previous publications have described the capture of mercury by scrubbing solutions containing oxidants. For instance Mendelsohn describes contacting elemental mercury containing flue gas with oxidizing solutions of halogens to effect mercury capture as a mercuric halide (Mendelsohn, M.H. 1999. "Method for the Removal of Elemental Mercury from a Gas Stream". United States Patent No. 5,900,042). This technique is not believed to be commercially viable for any or all of the following reasons:

- Mercury capture is inadequate. A maximum of 71.1% and 69.6% mercury removal was demonstrated for bromine and chlorine containing solutions respectively.
- Halogen reagents are wasted due to the undesirable consumption of halogen oxidant by sulphur dioxide in the flue gas.

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- Mercury capture does not utilize existing capital equipment including ESPs, FFs, BHs or FGDs. Expensive additional capital equipment is required. Addition of “bubblers” or liquid scrubbers into a coal-fired power plant would substantially increase pressure drops through the system thereby increasing equipment sizing requirements (e.g. air blowers). This would increase both capital and operating costs for the operation of air blowers.

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- Mercury capture, with the least expensive chlorine containing solutions, is reduced in the absence of nitric oxide. Clearly NO<sub>x</sub> removal by technology upstream of the bubbler such as selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) would dramatically reduce mercury removal further.

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- Previous systems for mercury control have been underutilized systems such as electrostatic precipitators (ESPs), wet flue gas desulphurization systems (FGDs), fabric filters (FFs) and baghouses (BHs) for mercury control. Such systems have suffered from a variety of mercury control related problems such as the following:

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- Injection of excessive levels of acid hydrogen chloride into real or simulated coal combustion flue gas resulting in destruction of alkaline solids able to capture mercury, especially oxidized mercury species such as mercuric chloride, and potential corrosion of metal surfaces such as steel surfaces found in power plants.

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- Use of excessive levels of expensive supplementary capital equipment and/or chemicals including wet scrubbers, photocatalysts, ultraviolet light generators, precious metals, activated carbon, chelates etc.

- 30
- Inadequate conversion of mercury to forms, such as mercuric halides for example mercuric chloride, adsorbable by alkaline solids such as alkaline

fly ash or alkali fused acidic fly ash to render it alkaline (e.g. bituminous coal fly ash).

## SUMMARY OF THE CURRENT INVENTION

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The current invention relates to the enhanced capture of mercury in coal combustion systems via enhanced conversion of mercury to mercuric halide species adsorbable by alkaline solids such as fly ash, alkali fused acidic ash (e.g. bituminous ash), dry FGD solids such as calcium oxide, calcium hydroxide or calcium carbonate in ESPs, FFs or BHs in the presence or absence of liquids such as wet FGD scrubber solutions. The current invention further relates to producing mercury containing fly ash, suitable for use in cementitious applications, thereby eliminating undesirable discharge of mercury to landfills from a fly ash source.

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According to the invention, there is provided a method of treating coal combustion flue gas, preferably that obtained after the "superheater" section of a coal-fired plant, for example the economizer inlet (Singer, Joseph G editor. 1991. Combustion Fossil Power. Combustion Engineering, Inc. Windsor, Connecticut, page 5-10), with a source of molecular halogen, such as chlorine gas or a thermolabile alkali metal hypohalite, for example calcium hypochlorite solution able to convert mercury rapidly to mercuric chloride, easily adsorbable by alkaline solids such as subbituminous fly ash, lignite fly ash, alkali fused bituminous fly ash or alkaline dry FGD solids capturable by ESPs, FFs, BHs alone or ahead of a liquid such as a wet FGD scrubbing liquor.

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Either molecular halogen such as chlorine gas, and/or bromine gas and/or iodine can be injected, or a molecular halogen precursor such as calcium hypochlorite can be injected into the flue gas. Molecular halogen precursors such as calcium hypochlorite can be used as a whole or partial source of the alkaline solids desirable for oxidized mercury absorption, e.g. mercuric halide such as mercuric

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chloride. Molecular halogen precursors containing calcium are particularly desirable in cases where the fly ash or alkali fused fly ash is intended to be used for cementitious applications e.g. in concrete or blended cements.

## 5 DETAILED DESCRIPTION

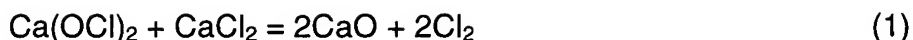
Molecular halogen sources such as chlorine gas, bromine gas or iodine can be used alone or in combination with molecular halogen precursors. Due to cost, chlorine gas is a preferred molecular halogen source.

Non-limiting examples of thermolabile halogen species, able to decompose thermally at flue gas temperatures, typical of coal-fired power plants, are shown in table 1 below:

**Table 1**

Thermolabile Halogen Precursor	Decomposition Temperature °C	Reference
Calcium hypochlorite	100	12 page 3.23
Magnesium bromide	165	13 page 969
Potassium tri-iodide	225	13 page 1320

Urano describes the thermal decomposition of calcium hypochlorite  $\text{Ca}(\text{OCl})_2$  quantitatively (Urano, Saburo. 1928. "Studies on Bleaching Powder, VII. The Decomposition of Calcium Hypochlorite by Heat in the Presence of Calcium Chloride". Journal of the Society of Chemical Industry of Japan. Volume 31, pages 46-52). He analyzed the products (in solid and gaseous states) after heating mixtures of calcium hypochlorite and calcium chloride  $\text{CaCl}_2$ . The decomposition of calcium hypochlorite in the presence of sufficient calcium chloride was chiefly according to the following reaction:



and partly to:



The evolution of chlorine was caused by the mutual reaction of calcium hypochlorite with calcium chloride. Molecular bromine can be generated by thermal decomposition of a dehydrated bromide salt solution in the presence of oxygen, for example magnesium bromide solution. Molecular iodine can be generated by thermal decomposition of a dehydrated iodide containing salt solution such as a potassium tri-iodide solution.

The conversion of mercury to its mercuric halide forms is thermodynamically favoured at temperatures typical of coal combustor flue gas, especially coal combustor flue gas between economizer inlets and ESPs, FGDs, BHs or FFs , as indicated by the negative values for the free energy of formation of mercuric halides, from elemental mercury and molecular halogen, in kilojoules/mole as a function of Celsius temperature as shown in the table 2 below, (Chase, M.W. et al. 1985. "JANAF Thermochemical Tables", third edition, Parts I and II, Journal of Physical and Chemical Reference Data, American Chemical Society and the American Institute of Physics for the Natural Bureau of Standards, Volume 14, Supplements I and II):

**Table 2**

	127°C	227°C	327°C	427°C	527°C
Mercuric bromide	-140	-126	-111	-91	-68
Mercuric chloride	-169	-148	-137	-120	-101
Mercuric iodide	-101	-92	-81	-58	-35

The larger the negative free energy of formation, the more likely the reaction is to proceed. Clearly from table 2, it can be seen that the formation of mercuric

chloride from elemental mercury and molecular chlorine is particularly favoured between 127 and 527°C typical of post-superheater coal combustor flue gas zones. This is fortunate, because the costs of molecular chlorine and molecular chlorine precursors, is lower than their bromine or iodine counterparts.

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The following examples illustrate the flexibility of the current invention and a rational, non-limiting basis for controlling mercury emissions via enhanced conversion of mercury to alkali adsorbable mercuric halide, especially mercuric chloride.

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#### Example 1 Enhancement of Mercury Capture by Subbituminous Coal Fly Ash

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Senior et al have estimated a rate constant  $k$  for the  $\text{Hg}^0 + \text{Cl}_2 = \text{HgCl}_2$  reaction of  $1.07 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1}$  at 500°C for an isothermal plug flow reactor (Senior, C.I. et al. 2000. "Gas-Phase Transformations of Mercury in Coal-Fired Power Plants". Fuel Processing Technology. 63:197-213). The room temperature rate for the same reaction is estimated at  $4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1}$ . The activation energy for the reaction was estimated at 3.7 kilojoules/mole.

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Galbreath and Zarlicke describe mercury species derived from combustion of subbituminous Absaloka PRB coal (see Galbreath et al., supra). This coal had  $50 \pm 10$  ppm chloride and  $0.052 \pm 0.005$  ppm mercury content with 0.57% sulphur. Absaloka coal combustion flue gas composition was 410 ppmv  $\text{SO}_2$ , 960 ppmv  $\text{NO}_x$  and 3 ppmv HCl. Baseline flue gas mercury emissions for this coal in  $\mu\text{g}/\text{m}^3$  were 2.28  $\text{Hg}^0$ , 1.06  $\text{HgX}_2$  (includes mercuric chloride), 2.26 Hg particulate and 5.53 mercury total. 100 ppmv HCl spiking of Absaloka coal combustion flue gas resulted in 1.21  $\text{HgX}_2$ . Senior et al have provided correlations between chloride content of coal, HCl and  $\text{Cl}_2$  emissions during coal combustion Senior et al., supra. Typically, 1% of the HCl injected converts to  $\text{Cl}_2$ , which means 0.5 ppmv  $\text{Cl}_2$  would create  $0.15 \mu\text{g}/\text{m}^3 \text{ HgCl}_2$ . Table 3 below illustrates mercury

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2017-2018-2019-2020-2021-2022-2023-2024-2025-2026-2027-2028-2029-2030-2031-2032-2033-2034-2035-2036-2037-2038-2039-2040-2041-2042-2043-2044-2045-2046-2047-2048-2049-2050-2051-2052-2053-2054-2055-2056-2057-2058-2059-2060-2061-2062-2063-2064-2065-2066-2067-2068-2069-2070-2071-2072-2073-2074-2075-2076-2077-2078-2079-2080-2081-2082-2083-2084-2085-2086-2087-2088-2089-2090-2091-2092-2093-2094-2095-2096-2097-2098-2099-2100-2101-2102-2103-2104-2105-2106-2107-2108-2109-2110-2111-2112-2113-2114-2115-2116-2117-2118-2119-2120-2121-2122-2123-2124-2125-2126-2127-2128-2129-2130-2131-2132-2133-2134-2135-2136-2137-2138-2139-2140-2141-2142-2143-2144-2145-2146-2147-2148-2149-2150-2151-2152-2153-2154-2155-2156-2157-2158-2159-2160-2161-2162-2163-2164-2165-2166-2167-2168-2169-2170-2171-2172-2173-2174-2175-2176-2177-2178-2179-2180-2181-2182-2183-2184-2185-2186-2187-2188-2189-2190-2191-2192-2193-2194-2195-2196-2197-2198-2199-2200-2201-2202-2203-2204-2205-2206-2207-2208-2209-2210-2211-2212-2213-2214-2215-2216-2217-2218-2219-2220-2221-2222-2223-2224-2225-2226-2227-2228-2229-2230-2231-2232-2233-2234-2235-2236-2237-2238-2239-2240-2241-2242-2243-2244-2245-2246-2247-2248-2249-2250-2251-2252-2253-2254-2255-2256-2257-2258-2259-2260-2261-2262-2263-2264-2265-2266-2267-2268-2269-2270-2271-2272-2273-2274-2275-2276-2277-2278-2279-2280-2281-2282-2283-2284-2285-2286-2287-2288-2289-2290-2291-2292-2293-2294-2295-2296-2297-2298-2299-2300-2301-2302-2303-2304-2305-2306-2307-2308-2309-2310-2311-2312-2313-2314-2315-2316-2317-2318-2319-2320-2321-2322-2323-2324-2325-2326-2327-2328-2329-2330-2331-2332-2333-2334-2335-2336-2337-2338-2339-2340-2341-2342-2343-2344-2345-2346-2347-2348-2349-2350-2351-2352-2353-2354-2355-2356-2357-2358-2359-2360-2361-2362-2363-2364-2365-2366-2367-2368-2369-2370-2371-2372-2373-2374-2375-2376-2377-2378-2379-2380-2381-2382-2383-2384-2385-2386-2387-2388-2389-2390-2391-2392-2393-2394-2395-2396-2397-2398-2399-2400-2401-2402-2403-2404-2405-2406-2407-2408-2409-2410-2411-2412-2413-2414-2415-2416-2417-2418-2419-2420-2421-2422-2423-2424-2425-2426-2427-2428-2429-2430-2431-2432-2433-2434-2435-2436-2437-2438-2439-2440-2441-2442-2443-2444-2445-2446-2447-2448-2449-2450-2451-2452-2453-2454-2455-2456-2457-2458-2459-2460-2461-2462-2463-2464-2465-2466-2467-2468-2469-2470-2471-2472-2473-2474-2475-2476-2477-2478-2479-2480-2481-2482-2483-2484-2485-2486-2487-2488-2489-2490-2491-2492-2493-2494-2495-2496-2497-2498-2499-2500-2501-2502-2503-2504-2505-2506-2507-2508-2509-2510-2511-2512-2513-2514-2515-2516-2517-2518-2519-2520-2521-2522-2523-2524-2525-2526-2527-2528-2529-2530-2531-2532-2533-2534-2535-2536-2537-2538-2539-2540-2541-2542-2543-2544-2545-2546-2547-2548-2549-2550-2551-2552-2553-2554-2555-2556-2557-2558-2559-2560-2561-2562-2563-2564-2565-2566-2567-2568-2569-2570-2571-2572-2573-2574-2575-2576-2577-2578-2579-2580-2581-2582-2583-2584-2585-2586-2587-2588-2589-2590-2591-2592-2593-2594-2595-2596-2597-2598-2599-2600-2601-2602-2603-2604-2605-2606-2607-2608-2609-2610-2611-2612-2613-2614-2615-2616-2617-2618-2619-2620-2621-2622-2623-2624-2625-2626-2627-2628-2629-2630-2631-2632-2633-2634-2635-2636-2637-2638-2639-2640-2641-2642-2643-2644-2645-2646-2647-2648-2649-2650-2651-2652-2653-2654-2655-2656-2657-2658-2659-2660-2661-2662-2663-2664-2665-2666-2667-2668-2669-2670-2671-2672-2673-2674-2675-2676-2677-2678-2679-2680-2681-2682-2683-2684-2685-2686-2687-2688-2689-2690-2691-2692-2693-2694-2695-2696-2697-2698-2699-2700-2701-2702-2703-2704-2705-2706-2707-2708-2709-2710-2711-2712-2713-2714-2715-2716-2717-2718-2719-2720-2721-2722-2723-2724-2725-2726-2727-2728-2729-2730-2731-2732-2733-2734-2735-2736-2737-2738-2739-2740-2741-2742-2743-2744-2745-2746-2747-2748-2749-2750-2751-2752-2753-2754-2755-2756-2757-2758-2759-2760-2761-2762-2763-2764-2765-2766-2767-2768-2769-2770-2771-2772-2773-2774-2775-2776-2777-2778-2779-2780-2781-2782-2783-2784-2785-2786-2787-2788-2789-2790-2791-2792-2793-2794-2795-2796-2797-2798-2799-2800-2801-2802-2803-2804-2805-2806-2807-2808-2809-2810-2811-2812-2813-2814-2815-2816-2817-2818-2819-2820-2821-2822-2823-2824-2825-2826-2827-2828-2829-2830-2831-2832-2833-2834-2835-2836-2837-2838-2839-2840-2841-2842-2843-2844-2845-2846-2847-2848-2849-2850-2851-2852-2853-2854-2855-2856-2857-2858-2859-2860-2861-2862-2863-2864-2865-2866-2867-2868-2869-2870-2871-2872-2873-2874-2875-2876-2877-2878-2879-2880-2881-2882-2883-2884-2885-2886-2887-2888-2889-2890-2891-2892-2893-2894-2895-2896-2897-2898-2899-2900-2901-2902-2903-2904-2905-2906-2907-2908-2909-2910-2911-2912-2913-2914-2915-2916-2917-2918-2919-2920-2921-2922-2923-2924-2925-2926-2927-2928-2929-2930-2931-2932-2933-2934-2935-2936-2937-2938-2939-2940-2941-2942-2943-2944-2945-2946-2947-2948-2949-2950-2951-2952-2953-2954-2955-2956-2957-2958-2959-2960-2961-2962-2963-2964-2965-2966-2967-2968-2969-2970-2971-2972-2973-2974-2975-2976-2977-2978-2979-2980-2981-2982-2983-2984-2985-2986-2987-2988-2989-2990-2991-2992-2993-2994-2995-2996-2997-2998-2999-3000-3001-3002-3003-3004-3005-3006-3007-3008-3009-3010-3011-3012-3013-3014-3015-3016-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emissions from subbituminous Absaloka coal (Galbreath, supra.). The upper part of the table shows measured mercury emissions derived from combustion of the coal. The bottom part of the table estimates elemental mercury conversion to mercuric chloride using 5 ppmv molecular chlorine injection into flue gas starting at 500°C. Of particular interest is the fact that 40% of the total mercury emission is unoxidized i.e. elemental mercury ( $2.21/5.53=40\%$ ) in the absence of the molecular chlorine spike. Reaction rate  $k$  is derived from data discussed previously (see Senior et al., supra.). Note that elemental mercury is estimated at only 2.9% of the baseline case ( $0.16/5.53=2.9\%$ ). Spiking of the flue gas of this subbituminous coal combustion, even at the low molecular chlorine level of 5 ppmv, results in substantial conversion of elemental mercury into the highly desirable, easily adsorbable, mercuric chloride form. Use of a thermolabile molecular chlorine precursor such as a solution of calcium hypochlorite and calcium chloride, able to generate alkaline solids such as calcium oxide CaO, enhances mercury capture in ESPs, FFs and BHs, for all of the reasons cited previously. Clearly, this method of mercury oxidation via molecular halogen sources, such as thermolabile calcium hypochlorite/calcium chloride aqueous mixtures, can be adjusted in numerous advantageous ways e.g. by varying (i) droplet size during injection into flue gas, (ii) concentration of thermolabile species, (iii) dosing level, etc. This technique complements current mercury capturing devices, having an alkaline subbituminous fly ash, including ESPs, FFs or BHs.

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Table 3

## Absaloka PRB

## Baselin

Hg total $\mu\text{g}/\text{m}^3$	5.53
Hg as $\text{HgX}_2$ $\mu\text{g}/\text{m}^3$	1.06
Hg as particulate $\mu\text{g}/\text{m}^3$	2.26
$\text{Hg}^\circ$ $\mu\text{g}/\text{m}^3$	2.21
% Hg elemental	40.0%

## Absaloka PRB

With  $\text{Cl}_2$   
spike  
At 5 ppmv

Hg total $\mu\text{g}/\text{m}^3$	5.53
Hg as $\text{HgX}_2$ $\mu\text{g}/\text{m}^3$	3.11
Hg as particulate $\mu\text{g}/\text{m}^3$	2.26
$\text{Hg}^\circ$ $\mu\text{g}/\text{m}^3$	0.16
% Hg elemental	2.9%
Ppm Hg total in coal	0.052

Time					$\text{Hg}^\circ$ initial	$\text{Cl}_2$ initial	$\text{Hg}^\circ$ reacted	% $\text{Hg}^\circ$
seconds	$^\circ\text{F}$	$^\circ\text{C}$	$^\circ\text{K}$	K	molecules/ $\text{cm}^3$	molecules/ $\text{cm}^3$	molecules/ $\text{cm}^3$	reacted
0.000	1000	538	811	1.09E-15	6.63E+09	1.34E+14		
0.100	964	518	791	1.08E-15	5.66E+09	1.34E+14	9.75E+08	15%
0.200	928	498	771	1.06E-15	4.84E+09	1.34E+14	8.20E+08	27%
0.300	892	478	751	1.05E-15	4.15E+09	1.34E+14	6.91E+08	37%
0.400	856	458	731	1.03E-15	3.56E+09	1.34E+14	5.83E+08	46%
0.500	820	438	711	1.01E-15	3.07E+09	1.34E+14	4.93E+08	54%
0.600	784	418	691	9.95E-16	2.65E+09	1.34E+14	4.18E+08	60%
0.700	748	398	671	9.76E-16	2.30E+09	1.34E+14	3.54E+08	65%
0.800	712	378	651	9.56E-16	2.00E+09	1.34E+14	3.01E+08	70%
0.900	676	358	631	9.35E-16	1.74E+09	1.34E+14	2.56E+08	74%
1.000	640	338	611	9.14E-16	1.52E+09	1.34E+14	2.19E+08	77%
1.100	604	318	591	8.92E-16	1.33E+09	1.34E+14	1.87E+08	80%
1.200	568	298	571	8.69E-16	1.17E+09	1.34E+14	1.60E+08	82%
1.300	532	278	551	8.44E-16	1.04E+09	1.34E+14	1.37E+08	84%
1.400	496	258	531	8.19E-16	9.20E+08	1.34E+14	1.18E+08	86%
1.500	460	238	511	7.93E-16	8.18E+08	1.34E+14	1.01E+08	88%
1.600	424	218	491	7.65E-16	7.31E+08	1.34E+14	8.72E+07	89%
1.700	388	198	471	7.36E-16	6.56E+08	1.34E+14	7.52E+07	90%
1.800	352	178	451	7.06E-16	5.91E+08	1.34E+14	6.49E+07	91%
1.900	316	158	431	6.74E-16	5.35E+08	1.34E+14	5.61E+07	92%
2.000	280	138	411	6.41E-16	4.87E+08	1.34E+14	4.85E+07	93%

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**Example 2   Enhancement of Mercury Capture by a Cementitious Fly Ash  
Derived from Fusion of Alkali with Bituminous Coal Ash  
During Combustion**

- 5   Table 4 below illustrates mercury emissions in lbs/hour as measured after an  
ESP, in a bituminous coal-fired combustor, with and without the addition of lime  
plus a lime flux as described in United States patent 6,250,235 (Oehr et al.). In  
this case the “additive” to coal ash ratio ranged from 0.81-0.85. Lime and flux  
represented 91% and 9% respectively of the additive formula. X-ray diffraction  
10   analysis of the fly ash resulting from the use of the “additive” indicated that the fly  
ash was cementitious and alkaline.

**Table 4**

Average Mercury Emissions by type with and without the Additive in lbs/hour

	Particulate	Oxidized	Elemental	Total
Baseline Average	3.15E-05	2.13E-03	3.93E-03	6.28E-03
% Mercury by type	1	34	63	100
Additive/Ash 0.81-0.85	1.55E-05	5.72E-04	2.86E-03	3.45E-03
% Mercury by type	0	17	83	100
% Mercury drop due to Additive	51	73	28	45

The results in the above table indicate two key factors:

- The cementitious alkaline fly ash resulting from the use of the additive is a  
20   good sorbent for oxidized mercury, because oxidized mercury emissions  
were reduced by  $(2.13-0.57)/2.13=73\%$  due to use of the additive.
- The flue gas lacked sufficient molecular halogen to effect substantial  
oxidation of elemental mercury (i.e. only 28% drop from baseline case).

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It is certain that injection of a molecular halogen source, such as calcium hypochlorite/calcium chloride aerosol or chlorine gas, at an appropriate dose, in the economizer/ESP section of this combustor, in similar fashion to Example 1, would effect substantial conversion of elemental mercury to easily adsorbable mercuric halide such as mercuric chloride. For instance, a 97.6% reduction in elemental mercury via its conversion to adsorbable mercuric chloride, in similar fashion to Example 1, without a corresponding increase in particulate and oxidized mercury would result in the following levels of mercury control vs. the baseline case shown in Table 5 below:

**Table 5**

Average Mercury Emissions by type with and without the Additive in lbs/hour

	Particulate	Oxidized	Elemental	Total
Baseline Average	3.15E-05	2.13E-03	3.93E-03	6.28E-03
% Mercury by type	1	34	63	100
Additive/Ash 0.81-0.85	1.55E-05	5.72E-04	6.86E-05	6.56E-04
% Mercury by type	2	87	10	100
% Mercury drop due to Additive	51	73	98	90

This 90% reduction in mercury emissions would satisfy EPA requirements without destroying the fly ash recyclability, caused by inappropriate injection of a sorbent such as activated carbon. The value of the United States 6,250,235 invention is clearly enhanced via the current invention. The technique described in the current example could also be applied ahead of other solids collection devices such as FFs and BHs.

### **Example 3    Enhancement of Mercury Capture from Bituminous Coal Combustion by FGDs**

A Canadian power plant burning high sulphur United States bituminous coal and equipped with a wet FGD reported the following mercury emissions at the ESP outlet and wet FGD outlet in  $\mu\text{g}/\text{m}^3$  shown in Table 6 below.

5

**Table 6**

<b>Bituminous Coal</b>	<b>Baseline ESP outlet</b>	<b>Baseline FGD outlet</b>
Hg total $\mu\text{g}/\text{m}^3$	<b>5.40</b>	<b>2.00</b>
Hg as $\text{HgX}_2$ $\mu\text{g}/\text{m}^3$	4.06	0.54
Hg as particulate $\mu\text{g}/\text{m}^3$	0.03	0.01
$\text{Hg}^0$ $\mu\text{g}/\text{m}^3$	<b>1.05</b>	<b>1.45</b>
% Hg removal via FGD		<b>63%</b>
% $\text{HgX}_2$ removal via FGD		<b>87%</b>

The data indicates that the FGD reduced mercury emissions 63% versus the ESP alone and reduced oxidized mercury emissions by 87%. Data indicates that (1.45-1.05)/4.06 = 10% of oxidized mercury input to the FGD was reconverted to elemental mercury. using a similar 5 ppmv molecular  $\text{Cl}_2$  spike as in analogous fashion to Example 1 above results in the following simulation shown in Table 7 below:

10

15

**Table 7**

<b>Bituminous Coal</b>	<b>Simulated ESP outlet</b>	<b>Simulated FGD outlet</b>
Hg total $\mu\text{g}/\text{m}^3$	<b>5.40</b>	<b>1.24</b>
Hg as $\text{HgX}_2$ $\mu\text{g}/\text{m}^3$	5.03	0.65
Hg as particulate $\mu\text{g}/\text{m}^3$	0.03	0.01
$\text{Hg}^0$ $\mu\text{g}/\text{m}^3$	<b>0.08</b>	<b>0.58*</b>
% Hg removal via FGD		<b>77%</b>
% $\text{HgX}_2$ removal via FGD		<b>87%</b>

\*assumes 10% of oxidized mercury input to FGD reconverted to elemental mercury.

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If elemental mercury formation inside the FGD is prevented using previous methods (e.g. Amrhein, Gerald et al.) then emissions are as shown in Table 8 below:

5

**Table 8**

<b>Bituminous Coal</b>	<b>Simulated ESP outlet</b>	<b>Simulated FGD outlet</b>
Hg total $\mu\text{g}/\text{m}^3$	<b>5.40</b>	<b>0.74</b>
Hg as $\text{HgX}_2$ $\mu\text{g}/\text{m}^3$	5.03	0.65
Hg as particulate $\mu\text{g}/\text{m}^3$	0.03	0.01
$\text{Hg}^0$ $\mu\text{g}/\text{m}^3$	<b>0.08</b>	<b>0.08*</b>
% Hg removal via FGD		<b>86%</b>
% $\text{HgX}_2$ removal via FGD		<b>87%</b>

\*assumes 100% inhibition of oxidized mercury conversion to elemental mercury.

Note that the techniques described above might be used in combination, to further enhance performance. For instance, the lime+flux ash fusion additive described in Example 2 above could be combined with the FGD system in Example 3 above plus the molecular halogen or thermolabile molecular halogen precursor of the current invention. This particular combination should easily achieve the 90% EPA mercury reduction requirement by trapping oxidized mercury in an alkaline fly ash thereby reducing oxidized mercury input to the FGD along with subsequent elemental mercury release. Alternatively, a small amount of subbituminous or lignite coal also capable of creating alkaline fly ash could be blended with bituminous coal to increase oxidized mercury capture in the ESP and subsequently reduce elemental mercury discharge from the FGD with or without techniques such as those described Amrhein, supra.

The above examples show that it is possible to achieve dramatic mercury emission reduction, through appropriate use of conventional installed equipment and techniques in combination with the teachings of the current invention. The above 3 examples are believed capable of achieving highly desirable conversion

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of elemental mercury to a mercuric halide, especially mercuric chloride, easily captured by existing pollution control devices including ESPs, BHs, FFs and wet or dry FGDs burning a variety of coals.

- 5 The above techniques can be used alone or supplemented with other techniques to enhance mercury capture in a cost effective way that eliminates undesirable contamination of fly ash with debris (e.g. activated carbon) rendering it unsuitable for recycling in cementitious applications.

- 10 Accordingly, while this invention has been described with reference to illustrative embodiments, this description is not intended to be construed in a limiting sense. Various modifications of the illustrative embodiments, as well as other  
15 claims will cover any such modifications or embodiments as fall within the true scope of the invention.

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